Ph.D. Synopsis submitted to

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"Growth and Characterization of ZnS_xSe_{1-x} Thin Films for Photoelectrochemical Solar Cell Applications"

For the Faculty of Science to be submitted in front of RRC

Abstract of proposed work plan/problem:

In present research work ZnS_xSe_{1-x}(Zinc Sulphoselenide) thin films will be grown onto amorphous and conducting glass substrates from a mixed solution of zinc chloride, thiourea and selenourea by simple **ChemicalSpray Pyrolysis Method**. Structural, morphological,compositional, optical,electrical andthermo electrical properties of the ZnS_xSe_{1-x}thinfilms will be studied by using XRD, SEM, FESEM, TEM, EDAX, UV–Vis spectroscopy, DC electrical resistivity measurement and photoelectrochemical characterization technique.

1. Introduction:

Zinc based II-VI wide-band-gap semiconductors offer opportunity for developing optoelectronic devices that can combine high sensitivity in the ultraviolet (UV) region with negligible sensitivity in the visible region. The II–VI compound semiconductors having wide band gap are promising materials for use in photovoltaic devices, blue light emitting diodes and laser diodes. In view of the fact that ZnS and ZnSe have practical applications, the study of the physical properties of their solid solution is of scientific interest. Solid solutions of ZnS_xSe_{1-x} compound appear to be very promising for various practical applications. In literature it is observed that the ZnS,ZnSeand ZnS_xSe_{1-x} thin films are the promising material as the buffer layer for CIGS solar cells.

ZnS_xSe_{1-x}thin films are not only non-toxic, but also increase the response in the short wavelength region. In this case, optical band gap, the lattice constant, RMS value and electron affinity of ZnS_xSe_{1-x} thin films can be adjusted by changing atom ratio of S to Se, which helps to enhance the blue response to the material.The electrical properties of ZnS_xSe_{1-x} materials depend on method of preparation and conditions of preparations. ZnS_xSe_{1-x} thin filmswill be grown by simple and low cost spray pyrolysis technique and its various properties will be studied.

2. Review of literature and development in the subject (Previous work done in the relevant area):

Vipin Kumar et al. [1] have prepared sintered ZnS_xSe_{1-x} films in the entire composition range from ZnSe to ZnS by using the screen printing technique. The band gap of these films is determined by reflection spectra in the wavelength range of 325-600nm using the Tauc relation.

These films showed a direct band gap, which varies from 3.50 eV for ZnS to 2.66 eV for ZnSe films. The wurtzite structure of ZnS_xSe_{1-x} films was confirmed by X-ray diffraction analysis of these films.

Agawane et al. [2] employed an environmentally benign chemical bath deposition (CBD) route to deposit zinc sulfide(ZnS) thinfilms. The CBD-ZnS thinfilms were further selenized in a furnace at various temperatures viz.200, 300, 400, and 500ºC and the S/(S + Se) ratio was found to be dependent on the annealingtemperature. Thefield emissionscanning electron microscopy and atomic force microscopy studies showed that all thefilms wereuniform, pin hole free, smooth, and adhered well to the glass substrate. The X-ray diffraction study on theZnSSe thinfilms showed the formation of the cubic phase, except for the unannealed ZnSSe thinfilm,which showed an amorphous phase. The tuning of the band gap energy of theZnSSe thinfilms was carried out by selenizing CBD-ZnS thinfilms, and as the S/(S + Se) ratio decreasedfrom 0.8 to 0.6, the band gap energy decreased from 3.20 to 3.12 eV.

Lai et al. [3] used molecular beam epitaxy (MBE) to grow the ZnSSe layers of the photodiodes on 2 inch GaP substrates.Wong and Coworkers [4] demonstrated that an autocorrelator based on two-photon absorption of ZnSSe photodetectors which is capable of measuring femtosecond laser pulses from 800 to 400 nm.JarkkoIhanuset al.[5] used Atomic Layer Epitaxy (ALE)techniqueto grow Polycrystalline $ZnS_{1-x}Se_x$ thin films from $ZnCl_2$, H_2S and Se on soda lime substrates.Shen Da-Ke et al. [6] studied the structural, optical and electrical properties of molecularbeam epitaxy (MBE) grown $ZnS_{0.8}Se_{0.2}$ thin films on indium tinoxide (ITO) glass substrates. They found that its characteristics depend on growth temperature.Khalid Shanzad and Diego J. Olego[7] demonstrated the effects of strain and carrier confinement in ZnSe- ZnS_xSe_{1-x} strained - layer super lattices.

D. Seghierand Coworkers [8] have studied the effect of hydrogenation on the electrical properties of N-doped ZnSe and ZnS_xSe_{1-x}thin films grown by molecularbeamepitaxy. It was observed that the hydrogenation of samples with a net acceptor density $10^{16}cm^{-3}$decreases the net acceptor density close to the surface and the peak height in deep-level transient spectra of thedominating nitrogen acceptor with activation energies 110 and 120meV in ZnSe and $ZnS_{0.08}Se_{0.82}$thin films,respectively. Samples with density in the 10^{17} cm^{-3} range did not exhibit such changes, while samples with density less than few times 10^{16} cm^{-3} became highly resistive.Liu et al. [9] have prepared the ZnS_xSe_{1-x} thin films by chemical bath deposition technique on glass substrates.Gavrishchuk et al. [10] have prepared monolithic ZnS_xSe_{1-x} layer by using Chemical Vapor Deposition (CVD) process.Ghassanand Coworkers [11] used

Cambridgeserial Total Energy Package (CASTEP) software for computation of stress-free crystal band gap $E_g$of materials in the systemZnS_xSe_{1-x} with a correction factor of 1.7.

Ganguly et al. [12] deposited ZnS_xSe_{1-x} ($0 < x < 1$) nanocrystalline films onto quartzsubstrates by a DC magnetron sputtering technique. The optical properties ofthe films were studied at room temperature (~300 K). The opticalabsorption was found to be dominated by the combined effects of opticallosses due to absorption and scattering. The absorption spectra indicated ablue shift.The electrical conductivity of the films was measured in the temperature range of 150–300 K. It was observed thatthe low-temperature conductivity could be explained by hooping of thecharge carriers in the coulomb gap, while at elevated temperature Mott'shooping was the predominant mode of conduction in these films. Chaudhari et al. [13] deposited ZnS_xSe_{1-x} thin films on GaAs(110) glass substrates. They described the growth of ZnS_xSe_{1-x} by a new chemical method and their characterization by transmission electron microscopy (TEM), X-ray Diffraction (XRD) and Small Angle X-Ray diffraction (SAXD) measurements.

Gabrel'yanand coworkers [14] studied the substitution in solid solutions $A_{II}B_{VI}$. It demonstrated the nonlinear dependence of the forbidden gap Eg on concentration. The Ab initio densities of states are calculated for the cubic modification of ZnS_xSe_{1-x} solid solutions (x = 0.0, 0.17, 0.33, 0.50, 0.67, 0.83, 1.0) in a virtual crystal approximation using the cluster version of the local coherent potential method in terms of full multiscattering theory. The chemical disordering effect was studied for a 50% solution with a sphalerite structure. The calculated optical deflection parameters are in good agreement with the experimental values and with the data obtained by other authors.

3.Objectives of research/Proposed hypothesis:

Objectives of present research work for the Ph.D. topic are

1)To grow good quality ZnS_xSe_{1-x}thin films by **Chemical Spray Pyrolysis Technique**,

2)To characterize ZnS_xSe_{1-x} thin films for various physical properties like structural,morphological, compositional,optical, electrical and thermoelectrical,

3)To study solar cell performance of ZnS_xSe_{1-x} thin filmsdeposited on conducting glass substrates in a photoelectrochemical cell using various electrolytes,

4)To study the effect of doping on the properties of ZnS_xSe_{1-x} thin films.

4.Methodology to be adopted:

For the growth of **ZnS_xSe_{1-x} thin films** the **Chemical Spray Pyrolysis**method will be used amongst the many methods available such as physical deposition, solution growth, sputtering, chemical bath deposition, electrochemical deposition, chemical vapour deposition, vacuum evaporation and Anodization.

The spray deposited films are in general strong and adherent, mechanically hard, pinhole free and stable with time and temperature. Spray pyrolysis is a cheap and facile method for the preparation of ZnS_xSe_{1-x} thin films. In this method, atomization provides a method to get droplets of precursor with very small sizes. As the droplets approach the substrate, the solvent vaporizes, the reactant diffuse to the substrate and a heterogeneous reaction occurs, which leads to the formation of thin films. In our present work, ZnS_xSe_{1-x} thin films will be prepared by chemical spray pyrolysis method. The various properties of deposited films such as structural, morphological, compositional and optical characteristics characterized by XRD, SEM, FESEM, TEM, EDAX,UV-Vis and electrical will be studied. The Photoelectrochemical properties of ZnS_xSe_{1-x} thin films will be studied. Also the effect of doingon the properties of ZnS_xSe_{1-x} thin films will be studied. The work will be divided in following manner:

a) Growth of Good Quality ZnS_xSe_{1-x}Thin Films:

It is proposed to grow ZnS_xSe_{1-x} thin films by **Chemical Spray Pyrolysis** method. At initial stages the efforts will be done to deposit good quality ZnS_xSe_{1-x} thin films on amorphous and conducting glass substrates by varying S:Se ratio. The various preparative parameters like concentration of precursor solution, thickness, substrate temperature and other parameters will be optimized to get good quality ZnS_xSe_{1-x}thin films.

b) Structural Studies:

The as deposited ZnS_xSe_{1-x} thin films will be characterized by X-Ray Diffraction (XRD) technique. The crystal structure, inter planar spacing, lattice planes, lattice parameters and crystallite size will be obtained and correlated with the film properties.

c) Morphological and Compositional Studies:

The morphology of the prepared ZnS_xSe_{1-x} thin films will be studied by using Scanning Electron Microscopy (SEM) or Atomic Force Microscopy (AFM). The grain size, surface roughness, porosity will be studied using SEM and AFM techniques.

The Compositional Analysis of as deposited ZnS_xSe_{1-x}thin films will be studied by using Energy Dispersive Analysis by X–Rays (EDAX) technique. The correlation between as taken composition and film composition will be obtained.

d) Optical Studies:

The optical absorption of ZnS_xSe_{1-x} thin films will be obtained by using UV–Vis (UltraViolet–Visible) spectrophotometer. The coefficient of absorption, band gap energy (Eg), nature of transition, power factor will be obtained from optical absorption spectra.

e) Electrical and Thermoelectrical Studies:

The electrical resistivity measurements of as deposited ZnS_xSe_{1-x} thin films will be carried out by using DC two point probe method. The room temperature resistivity, activation energy will be obtained and correlated with film properties. The thermoelectric power measurement studies will be carried out in order to study the type of conductivity exhibited by ZnS_xSe_{1-x} thin films.

f) Photoelectrochemical Studies:

In order to find the applications of ZnS_xSe_{1-x} thin films, the ZnS_xSe_{1-x}thin films deposited on conducting glass substrates will be used as active photoelectrode in Photoelectrochemical (PEC) solar cells. The various cell parameters of PECcells like Junction Identity Factor in Dark and under Illumination, Short Circuit Current, (Isc) Open Circuit Voltage (Voc), Fill Factor, Efficiency, Series Resistance and Shunt Resistance will be obtained.The PEC Cell will be studied for capacitance-voltage (C-V) characteristics, power output characteristics and spectral response characteristics.

g) Effect of Doping:

In order to study the effect of technical parameters, the ZnS_xSe_{1-x} films will be doped with traces of impurity and studied for all above mentioned characteristics.

5.Importance of the study/Society application:

Semiconductor nanostructured thin films are of current interest due tothe variation of their bulk properties. A key aspect of semiconductors in a nanocrystallinethin-film form is the modification of the energy levels and thedensity of states owing to the confinement of the charge carriers.Nanocrystalline II–VI semiconductors have already indicatedimproved linear and nonlinear optical responses with potential application in various fields.Theexperimental observations published so far on nanocrystallinesemiconducting materials have mainly been on elemental orbinary compound semiconductors. In recent times, ZnSe andZnS_xSe_{1-x} alloys have been extensively studied forthe realization of blue-light emitting diodes (blue-LEDs), laser diodes, photovoltaic devices, optoelectronic devices, radiation detectors, thermoelectric devices and solar cells. The effective control of the electrical propertiesthrough doping (especially p-type) is the key issues ofresearch before the materials could be fruitfully utilized indevice technology.

As considering the above view, the properties of ZnS_xSe_{1-x} thin films will be studied thoroughly in the present work for societal applications like solar cells.

6.Proposed work plan/ formulation and structure of study:

Plan of work and targets to be achieved during First Year:

During the first year of researchwork;an effort will be made to collect more information related to the present work using different books, research papers and journals. Also efforts will be done to grow good quality ZnS_xSe_{1-x} thin films using various chemicals like zinc chloride, thiourea and selenourea. Two progress reports will be submitted at the end of this year.

Plan of work and targets to be achieved duringSecondYear:

During second year, all preparative parameters will be optimized in order to get good photoactive ZnS_xSe_{1-x} thin films. All deposited films will be characterized by various techniques such as XRD, SEM, FESEM, TEM, EDAX, UV–Vis, DC electrical resistivity and photoelectrochemical technique. Also we will try to submit two or more research papers to reputed international research journals. Two progress reports will be submitted at the end of this year.

Plan of work and targets to be achieved duringThirdYear:

During this year; thesis writing will be started and publication of two research papers on ZnS_xSe_{1-x} thin films in reputed journals will be undertaken. Also the research work will be presented in national, international seminars, workshops and conferences. Thesis will be submitted to the university.

7. References:

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